

VERIFICATION OF TRANSLATION

I, Shiho Watanabe, translator of 6F Yodagawa 5-Bankan, 3-2-1, Toyosaki, Kita-ku, Osaka, Japan, hereby declare that I am conversant with the English and Japanese languages and am a competent translator thereof. I further declare that to the best of my knowledge and belief the following is a true and correct translation made by me of Japanese Patent Application No. 2002-293857 filed on October 7, 2002.

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[RECEIPT NO.] 011305

[AMOUNT] 21,000 yen

[LIST OF ENCLOSURES]

Specification 1

15 Drawings 1

Abstract 1

[POWER OF ATTORNEY NO.] 9809938

[DOCUMENT] Specification

[TITLE OF THE INVENTION] PHOSPHOR TREATMENT METHOD AND TREATMENT
APPARATUS FOR THE SAME

5 [CLAIMS]

[CLAIM 1]

A phosphor treatment method including a step of performing
modification such that (i) a phosphor is impregnated with a gas
atmosphere including at least one of ozone, oxygen and monatomic
10 oxygen, (ii) a surface of the phosphor and a vicinity of the surface
chemically react with at least one of the ozone, the oxygen and
the monatomic oxygen, and (iii) an oxygen element ratio of the surface
of the phosphor and the vicinity of the surface is higher than an
oxygen element ratio of the phosphor except for the surface of the
15 phosphor and the vicinity of the surface.

[CLAIM 2]

A phosphor treatment method including a step of performing
modification such that (i) a phosphor is impregnated with a mixed
gas atmosphere including at least one of ozone, oxygen and monatomic
20 oxygen, and monatomic fluorine, (ii) a surface of the phosphor and
a vicinity of the surface chemically react with at least one of
the ozone, the oxygen and the monatomic oxygen, and monatomic
fluorine, (iii) an oxygen element ratio of the surface of the phosphor
and the vicinity of the surface is higher than an oxygen element
25 ratio of the phosphor except for the surface of the phosphor and
the vicinity of the surface, and (iv) a fluorine element ratio of
the surface of the phosphor and the vicinity of the surface is higher

than a fluorine element ratio of the phosphor except for the phosphor surface and the vicinity of the surface.

[CLAIM 3]

5 The phosphor treatment method of one of Claims 1 and 2, wherein the mixed gas atmosphere is heated.

[CLAIM 4]

The phosphor treatment method of Claims 3, wherein the mixed gas atmosphere is heated at 300 °C or lower.

[CLAIM 5]

10 The phosphor treatment method of Claim 3, wherein the mixed gas atmosphere is heated at 100 °C or lower.

[CLAIM 6]

15 The phosphor treatment method of one of Claims 3 to 5, wherein the mixed gas atmosphere is heated so as to be maintained for a predetermined period of time at a predetermined temperature.

[CLAIM 7]

The phosphor treatment method of one of Claims 3 to 6, wherein the mixed gas atmosphere has a process in which a temperature rises.

20 [CLAIM 8]

The phosphor treatment method of one of Claims 1 to 7, wherein the mixed gas atmosphere is exposed to ultraviolet light.

[CLAIM 9]

25 The phosphor treatment method of Claim 8, wherein the ultraviolet light has two or more kinds of different wavelengths.

[CLAIM 10]

The phosphor treatment method of one of Claims 8 and 9, wherein the ultraviolet light is not applied to the surface of the phosphor.

[CLAIM 11]

5 The phosphor treatment method of one of Claims 1 to 10, wherein the mixed gas atmosphere includes inert gas.

[CLAIM 12]

 The phosphor treatment method of one of Claims 1 to 11, wherein the phosphor is an oxide phosphor.

10 [CLAIM 13]

 The phosphor treatment method of one of Claims 1 to 12, wherein the phosphor includes one of a manganese ion and a rare-earth ion.

[CLAIM 14]

15 The phosphor treatment method of one of Claims 1 to 13, wherein the phosphor includes aluminate and an europium ion.

[CLAIM 15]

 The phosphor treatment method of Claim 2, wherein fluorinated gas is CF_4 .

20 [CLAIM 16]

 The phosphor treatment method of one of Claims 1 to 15, wherein the phosphor is used for an image display apparatus.

[CLAIM 17]

 The phosphor treatment method of Claim 16, wherein
25 the phosphor is used for a plasma display.

[CLAIM 18]

 The phosphor treatment method of one of Claims 1 to 15, wherein

the phosphor is used for an illumination device.

[CLAIM 19]

The phosphor treatment apparatus using the phosphor treatment method of one of Claims 1 to 18.

5 [CLAIM 20]

A phosphor treatment method including a step of performing modification such that (i) a phosphor is impregnated with a mixed gas atmosphere including at least monatomic fluorine, (ii) a surface of the phosphor and a vicinity of the surface chemically react with
10 at least monatomic fluorine, and (iii) a fluorine element ratio of the surface of the phosphor and the vicinity of the surface is higher than a fluorine element ratio of the phosphor except for the surface of the phosphor and the vicinity of the surface.

[DETAILED DESCRIPTION OF THE INVENTION]

15 [0001]

[FIELD OF THE INVENTION]

The present invention relates to phosphors used in a plasma display panel (PDP) used as a display or the like of a color TV receiver or in an illumination device.

20 [0002]

[DESCRIPTION OF THE RELATED ART]

A phosphor treatment method in which the phosphors are heat-treated (i.e. fired) at a high temperature of approximately 1100 °C to improve the crystallinity and enhance characteristics
25 is well known. In general, a phosphor and a binder are mixed and processed to a paste, and the resultant paste is applied onto a substrate. However, a heat treatment is performed at several hundred

degrees to eliminate moisture in the binder in order to obtain a long lasting phosphor.

[0003]

Also, as a method of forming a long lasting phosphor, there is a method of enhancing characteristics by preventing moisture absorption which causes deterioration in luminance by manufacturing a protective coating layer on a surface of a phosphor. For example, as a method of forming a lamp of an EL phosphor which is coated, a treatment method of supplying a coating precursor (trimethyl aluminum) and mixed gas composed of oxygen and ozone into a reactor vessel, and spending a considerable amount of time to coat phosphor particles (see Patent Document 1, for example).

[0004]

In a plasma display panel (PDP) that performs a full color display by causing phosphors of three colors to emit light by exciting ultraviolet light by discharge, phosphors are formed by the following processes. FIG. 5 shows a schematic cross-sectional diagram showing one example of an AC-driven PDP having a general three-electrode structure. In the present diagram, formed on a front glass substrate 13 are display electrodes 14 that are covered by a dielectric glass layer 15 and a magnesium oxide (MgO) dielectric protective layer 16.

[0005]

On a rear glass substrate 17, on the other hand, address electrodes 18 and barrier ribs 19 are disposed, and each of phosphor layers 21-23 of respective colors (red, green, and blue) is provided in a space between two adjacent barrier ribs 19.

[0006]

The front glass substrate 13 as formed above is disposed on the barrier ribs 19 arranged on the rear glass substrate 17, and discharge gas is filled between these substrates 13 and 17 to form a discharge space 20.

[0007]

In this PDP, vacuum ultraviolet light (predominantly, a wavelength of 147 nm) is generated through an electric discharge in the discharge space 20, and each of the phosphor layers 21-23 is excited to thereby emit light, which results in a display in colors.

[0008]

The above PDP can be manufactured as follows.

[0009]

A silver paste is applied to the front glass substrate 13, and then fired to form the display electrodes 14. Further, a dielectric glass paste is applied, and then fired to form a dielectric glass layer 15, on which a protective layer 16 is formed.

[0010]

Onto the rear glass substrate 17, on the other hand, a silver paste is applied and fired to form the address electrodes 18. Next, a glass paste is applied at predetermined intervals, and then fired to form the barrier ribs 19. Subsequently, the phosphor layers 21-23 are formed by respectively applying phosphor pastes of individual colors to the spaces between the barrier ribs 19, and firing the phosphor pastes at around 500 °C to remove resin components and the like therefrom.

[0011]

After this firing process for forming the phosphor layers 21-23, sealing glass frits are applied around the edge of the rear glass substrate 17 to herewith form a sealing glass layer, and calcinated
5 at around 350 °C in order to remove resin components and such from the formed sealing glass layer (frit calcination process).

[0012]

Then, the front glass substrate 13 and the rear glass substrate 17 are laid on top of each other so that the display electrodes
10 14 and the address electrodes 18 face at right angles to one another. These superimposed glass substrates are attached and sealed by heating at a temperature (approximately 450 °C) higher than the softening temperature of the sealing glass (sealing process).

[0013]

15 Subsequently, as the sealed panel formed of the front and rear glass substrates 13 and 17 is heated up to around 350 °C, air is evacuated from the internal space formed between the both glass substrates, i.e. the space which is formed between the front and rear glass substrates 1 and 5, and to which the phosphor layers
20 are exposed (evacuation process). After the evacuation process is completed, discharge gas is introduced to the space until the pressure reaches a predetermined point (normally, 300 Torr - 500 Torr) ..

[0014]

25 Patent document 1: Japanese Laid-open application 2000-96044

[0015]

[PROBLEM TO BE SOLVED BY THE INVENTION]

In the PDP described as the conventional technology in the above, it has been important to improve the luminescent characteristics, including the luminance. Especially, a quality assurance period of a PDP depends on time-lapse changes in luminescent characteristics of phosphors used in a luminous display unit.

[0016]

Due to moisture, application of heat or the like in the PDP manufacturing process, the luminance of phosphors deteriorates and the chromaticity of the phosphors also changes. Therefore, the time-lapse changes in phosphors during the PDP manufacturing process leads to a degradation of characteristics of a panel. In addition, the phosphor layers are exposed to plasma associated with an electric discharge during the time when the PDP is in operation, which results in time-lapse changes in phosphor layers over time. Therefore, a phosphor having small time-lapse changes due to the manufacturing process of a PDP and a PDP operation are big challenges.

[0017]

With the method of treating the coated phosphor using ozone and oxygen shown as a conventional example, it is possible to improve luminance. However, this method is not effective for preventing changes in chromaticity.

[0018]

The present invention has an object to manufacture a PDP that suppresses the time-lapse changes in luminescent characteristics of the phosphor and has excellent luminescent characteristics.

[0019]

[MEANS TO SOLVE THE PROBLEMS]

In order to solve the above problems, the phosphor and the treatment method for the same have the following structure. That is, the phosphor treatment method of Claim 1 includes a step of performing modification such that (i) a phosphor is impregnated with a gas atmosphere including at least one of ozone, oxygen and monatomic oxygen, (ii) a surface of the phosphor and a vicinity of the surface chemically react with at least one of the ozone, the oxygen and the monatomic oxygen, and (iii) an oxygen element ratio of the surface of the phosphor and the vicinity of the surface is higher than an oxygen element ratio of the phosphor except for the surface of the phosphor and the vicinity of the surface.

[0020]

Also, The phosphor treatment method of claim 2 includes a step of performing modification such that (i) a phosphor is impregnated with a mixed gas atmosphere including at least one of ozone, oxygen and monatomic oxygen, and monatomic fluorine, (ii) a surface of the phosphor and a vicinity of the surface chemically react with at least one of the ozone, the oxygen and the monatomic oxygen, and monatomic fluorine, (iii) an oxygen element ratio of the surface of the phosphor and the vicinity of the surface is higher than an oxygen element ratio of the phosphor except for the surface of the phosphor and the vicinity of the surface, and (iv) a fluorine element ratio of the surface of the phosphor and the vicinity of the surface is higher than a fluorine element ratio of the phosphor except for the phosphor surface and the vicinity of the surface.

[0021]

Also, the mixed gas atmosphere is heated.

[0023]

Also, the mixed gas atmosphere is heated at 300 °C or lower.

[0024]

5 Also, the mixed gas atmosphere is heated at 100 °C or lower.

[0025]

Also, the mixed gas atmosphere is heated so as to be maintained for a predetermined period of time at a predetermined temperature.

[0026]

10 Also, the mixed gas atmosphere has a process in which a temperature rises.

[0027]

Also, the mixed gas atmosphere is exposed to ultraviolet light.

15 [0028]

Also, the ultraviolet light has two or more kinds of different wavelengths.

[0029]

20 Also, the ultraviolet light is not applied to the surface of the phosphor.

[0030]

Also, the mixed gas atmosphere includes inert gas.

[0031]

Also, the phosphor is an oxide phosphor.

25 [0032]

Also, the phosphor includes one of a manganese ion and a rare-earth ion.

[0033]

Also, the phosphor includes aluminate and an europium ion.

[0034]

Also, fluorinated gas is CF_4 .

[0035]

5 Also, the phosphor is used for an image display apparatus.

[0036]

Also, the phosphor is used for a plasma display.

[0037]

Also, the phosphor is used for an illumination device.

10 [EMBODIMENTS OF THE INVENTION]

The following describes embodiments of the present invention referring to drawings.

[0038]

First embodiment

15 The phosphor of the present invention is composed of (i) a modified portion which is a portion (a) including a surface of the phosphor and a vicinity of the surface (b) and having an oxygen element ratio that is different from an oxygen element of the phosphor except for the surface of the phosphor and the vicinity
20 of the surface, and (ii) a region of the phosphor except for the surface of the phosphor and the vicinity of the surface. Here, the surface of the phosphor is impregnated with ozone and monatomic oxygen. A region of the phosphor to be modified for suppressing time-lapse changes need only be a light-emitting portion of the
25 phosphor. However, the light-emitting portion changes according to the time-lapse changes. Therefore, it is preferable that the region to be modified is sufficiently large.

[0039]

— An excitation region of the phosphor is different according to energy to be excited. Especially, in a PDP, the phosphor layer is mainly excited by vacuum ultraviolet light. Therefore, only the surface of the phosphor layer and a vicinity of the surface are excited. Therefore, since a surface part of the phosphor layer is mainly modified in the present invention, it is very effective for a phosphor used in a PDP in which a light-emitting region is the surface of the phosphor.

[0040]

For example, a luminescent center is an Europium (Eu) in $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+}$ (hereinafter, BAM) which is a blue phosphor material generally used in a PDP. In order to prevent an oxidization of this Eu, BAM is synthesized in an oxygen reduction atmosphere. Therefore, many oxygen vacancies exist in crystals of BAM. These oxygen vacancies often cause time-lapse changes. In particular, when portions in which oxygen vacancies are formed absorb moisture, chromaticity which is a luminescent characteristic of BAM changes. Also, the moisture absorption accelerates deterioration in luminance during operation of the PDP. Furthermore, when moisture attaches to a phosphor, moisture is brought into an inner part of a complete panel, affecting a PDP operation. Therefore, BAM having few oxygen vacancies is preferred as a phosphor used in a PDP.

[0041]

With the phosphor treatment method of the present invention, it is possible to realize BAM having few time-lapse changes by causing a chemical reaction between oxide in a reactive state and a phosphor

by using gas in which oxygen atoms are included in introduced gas, and therefore compensating oxygen vacancies on a surface layer of BAM.

[0042]

5 For example, oxide radicals generated by generation of ozone and break-down of ozone are brought into a reactive state by applying ultraviolet light in an oxide atmosphere. This oxide brought into the reactive state chemically reacts with a phosphor, which modifies the phosphor.

10 [0043]

FIG.1 shows the first embodiment of the present invention. 1 is a reactor vessel, 2 is an oxygen gas inlet, 3 is a phosphor, 4 is a processing object on which a phosphor is attached, 5 is a sample stage, 6 is a UV lamp, 7 is a nitrogen gas inlet, 8 is a gas outlet for discharging gas, 9 is UV light, 10 is a temperature controller, and 11 is a UV lamp controller. Note that the processing object 4 may be composed of only the phosphor 3.

[0044]

20 The processing object 4 on which the phosphor 3 is attached is positioned on the sample stage 5 in the reactor vessel 1. The phosphor 3 may be mounted on the processing object 4 in a powder form, or may be in a phosphor layer state in which the phosphor 3 is applied on the processing object 4. Also, the phosphor 3 does not have to be put on the processing object 4, and may be directly put on the sample stage 5.

25 [0045]

For example, the processing object 4 may be manufactured by

mixing a phosphor in a powder state that is made up of aluminate and europium ions (BAM, short for $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+}$) as a blue phosphor with a binder of a desired viscosity, and applying the resultant mixture on a quartz substrate.

5 [0046]

After supplying a sufficient amount of nitrogen from the nitrogen gas inlet 7, the sample stage 5 is heated to 300°C by the temperature controller 10. When the temperature reaches 300°C , nitrogen gas is stopped and oxygen is supplied from the oxide gas
10 inlet 2 at a rate of 1L/min. Introduced gases of nitrogen and oxygen are discharged from the outlet 8. When the oxygen gas has been fully distributed inside the reactor vessel 1, the UV lamp 6 is caused to emit light for 30 minutes.

[0047]

15 After the light emission, the oxide gas is stopped, the nitrogen gas is supplied into the reactor vessel 1, and the sample stage 5 is cooled to room temperature.

[0048]

The following describes the process in which ozone and
20 monatomic oxygen are generated by an application of UV light to oxygen of the introduced gas. When a light ray having a very short wavelength in the UV range, called an ozone producing radiation, is applied to oxygen (O_2) introduced to the reactor vessel 1, molecular oxygen (O_2) is split into two oxygen atoms (O). Then, each of these
25 oxygen atoms (O) combines with other molecular oxygen to form ozone (O_3). Also, since ultraviolet light has light ray having a wavelength that breaks ozone down, the oxygen atoms (O) formed in the above

decomposition reaction react with the formed ozone, and break the ozone down to further form monatomic oxygen.

[0049]

That is, the surface of the phosphor chemically reacts with monatomic oxide molecular ozone formed at the time of generating and breaking down monatomic oxygen which is formed at the time of generating and breaking down ozone. This fills oxygen vacancies on the surface of the phosphor, which modifies the phosphor.

[0050]

Note that the UV lamp 6 may apply radiation with a wavelength at which ozone is produced (1849 angstrom) and radiation with a wavelength at which ozone is broken down (2537 angstrom), for example, at the same time. Alternatively, the UV lamp 6 having a wavelength having a high light-emission peak may be used.

[0051]

Also, since ozone is very unstable, impurities on and around the surface of the phosphor chemically react with ozone, which eliminates factors that accelerate time-lapse changes. For example, ozone chemically reacts with carbon atoms that exist on and around the surface of the phosphor to form carbon oxide which can be eliminated.

[0052]

The UV light 9 is absorbed, to some extent, by oxygen before reaching the surface of the phosphor 3. However, as mentioned above, the phosphor deteriorates because of ultraviolet light. The UV light 9 is set so as not to be directly applied to the phosphor 3. For example, a shutter for blocking off the UV light 9 may be provided

above the processing object 4 only when the UV light 9 is applied.
A plate made of ceramic material or the like may be used for covering
the phosphor 3 so as not to be in contact with the phosphor 3.

[0053]

5 Also, a chemical reaction may be accelerated by heating mixed
gas atmosphere while applying the UV light. For example, a phosphor
and mixed gas atmosphere can be heated by directly placing the
phosphor on a hot plate or the like, and heating the hot plate.

[0054]

10 In order to show the effect of this heat treatment, a description
is given of a deterioration experiment of the phosphor at high
temperature and humid atmosphere. A testing sample was manufactured
by applying a BAM phosphor on a quartz substrate, and a treatment
was performed on the surface using a commercially available ozone
15 generator by changing a temperature of a sample stage. The testing
sample was provided in a reactor vessel of the ozone generator,
and nitrogen was supplied until a temperature reaches a predetermined
temperature. Then ozone was generated for 30 minutes after the
temperature of the substrate was stabilized. Subsequently, nitrogen
20 was introduced, replacing the oxygen, to cool down the reactor vessel.
After the treatment was performed on the surface, the phosphor layers
were exposed to a humidified atmosphere of approximately 450 °C
with the use of a tubular duct. Thus, the phosphor layers were
made to deteriorate at an accelerating rate, and characteristics
25 of chromaticity and luminescence intensity after the treatment were
measured.

[0055]

FIG. 2 shows the result of deterioration in chromaticity. A horizontal axis represents a temperature of the sample stage in the process of treating the surface of the phosphor, and a vertical axis represents chromaticity y . A solid line denotes chromaticity y after the process of treating a surface of a phosphor and a dash line denotes chromaticity y prior to the deterioration test. "Chromaticity y " is a y -value on an x - y chromaticity coordinate plane which represents a two-dimensional color space according to the CIE standard colorimetric system. As a blue phosphor deteriorates, the y -value largely changes while the x -value shows small changes, and therefore the y -value was used as the assessment criterion. After treating the surface, as a heating temperature becomes higher, a characteristic closer to an initial state of the testing sample can be obtained. Therefore, since a reaction is accelerated by the heat treatment, oxygen vacancies on the surface of the phosphor can be filled in a short period of time, which enhances the characteristics of the phosphor.

[0056]

In particular, if the phosphor is heated to 300 °C, the same chromaticity as an initial chromaticity can be obtained, making it possible to obtain a phosphor having preferable characteristics.

[0057]

FIG. 3 shows deterioration in luminescence intensity. A horizontal axis represents a temperature for a treatment, and a vertical axis represents a luminescence intensity ratio between a value after the deterioration treatment and an initial value when no deterioration treatment is performed. As the heating temperature

increases, the oxidation of Eu accelerates and the luminescence intensity decreases. However, by setting the heating temperature for the treatment low, it is possible to suppress deterioration in luminance, and to enhance the chromaticity. In particular, when the heating temperature for the treatment is under 100 °C, there is little change in the luminescence intensity, which makes it possible to obtain a phosphor having preferable characteristics.

[0058]

Therefore, when the heating temperature for the treatment is as high as around 300 °C, it is possible to enhance the chromaticity without deteriorating the luminescence intensity if the treatment is performed for a short period of time less than 30 minutes. Also, when the heating temperature is as low as around 100 °C, the reaction rate can be reduced by performing the treatment on the surface for a long time so that monatomic oxygen is distributed, within each of the phosphors, only to a shallow region from the surface. This prevents oxidation of Eu and enhances the chromaticity. For example, the phosphor needs to be treated at a reactive atmosphere at 100 °C for six hours.

[0059]

Also, as shown in the above example, a phosphor having favorable characteristics can be produced at a high yield over a short time period in a stable manner by supplying mixed gas during only a stabilization period of the heat treatment (Claim 6).

[0060]

Furthermore, it is possible to fill oxygen vacancies formed on the surface of the phosphor, and to mitigate luminance degradation

due to oxidation of Eu by decelerating the reaction rate by gradually increasing the temperature from a room temperature to a high temperature of approximately 300 °C.

[0061]

5 Also, the reaction rate may be reduced by introducing inert gas, such as nitrogen, into a mixed gas atmosphere.

[0062]

10 Conventionally, it has taken time to cool off the phosphor since characteristics were enhanced by firing the phosphor at around 1100 °C. However, in the present invention, since the treatment is performed at a low temperature, it is possible to manufacture a phosphor easily, which shortens processing time and reduces the cost.

[0063]

15 Also, the treatment performed on the surface of the phosphor is very effective for oxide phosphors on which oxygen vacancies easily formed, and deterioration in luminance can be smaller by using, as the luminescent center, manganese ions or rare-earth ions that can obtain high luminous efficiency. In particular, the phosphor
20 treatment method of the present invention is exceptionally effective for BAM used as a blue phosphor having marked time-lapse changes, and makes it possible to obtain preferable characteristics.

[0064]

25 Such phosphors are practical in an illumination device, or an image display apparatus such as plasma display or the like.

[0065]

For example, in the case of the plasma display, phosphor pastes

are applied after forming address electrodes and the spaces between the barrier ribs on a rear substrate. Ozone and monatomic oxygen are generated by providing this rear substrate in a reactor vessel, introducing oxygen, heating the inside of the reactor vessel at 300 °C, and then having a Xe excimer lamp emit light for 30 minutes. This fills the oxygen vacancies of the phosphor, making it possible to obtain a phosphor characteristic which is tolerant of moisture absorption. Since there are three kinds of phosphors, a red phosphor, a green phosphor and a blue phosphor, these phosphors may be treated at the same time, or the above-stated ozone process may be performed after the blue phosphor is applied.

[0066]

Second embodiment

FIG.4 shows a second embodiment of the present invention. 1 is a reactor vessel, 2 is an oxide gas inlet, 3 is a phosphor, 4 is a processing object on which the phosphor is attached, 5 is a sample stage, 6 is a UV lamp, 7 is a nitrogen gas inlet, 8 is a gas outlet that discharges gas, 9 is UV light, 10 is a temperature controller, 11 is a UV lamp controller and 12 is a fluorinated gas inlet. Note that, the processing object 4 may be composed of only the phosphor 3.

[0067]

As with the first embodiment, the processing object 4 on which the phosphor 3 is attached is placed on the sample stage 5 in the reactor vessel 1. After supplying sufficient amount of nitrogen from the nitrogen gas inlet 7, the sample stage 5 is heated using the temperature controller 10 to around 150 °C. When a temperature

reaches 150 °C, nitrogen gas is stopped. Then, oxygen and fluorinated gas are supplied from the oxide gas inlet 2 and the fluorinated gas inlet 12, respectively, and mixed gas of oxygen and fluorinated gas is supplied to the reactor vessel 1. Although fluorinated gas, for example, includes CF₄, SF₆ and the like, a description is given using CF₄ here.

[0068]

The flow volume ratio of oxygen gas and CF₄ of the mixed gas may be approximately 1 : 1. Introduced nitrogen, oxygen and CF₄ are flown out from the gas outlet 8. Once oxygen and CF₄ have been fully distributed inside the reactor vessel 1, the UV lamp 6 applies UV light to the introduced oxygen and CF₄ for about 30 minutes. Generation and break-down of ozone of oxygen are caused at the same time by the UV light 9, which generates monatomic oxygen. The phosphor is impregnated with a reactive gas including generated radical monatomic oxygen, which fills oxygen vacancies, modifying the surface of the phosphor. Also, the phosphor is reacted with carbon of CF₄ gas by ozone and monatomic oxygen to form carbon dioxide, and fluorine atoms react with the surface of the phosphor, which modifies the surface of the phosphor to have water repellency.

[0069]

As with the first embodiment, oxygen gas is stopped after the treatment on the surface ends, nitrogen gas is supplied to the reactor vessel 1, and the sample stage 5 is cooled off to a room temperature.

[0070]

As mentioned above, a fluorine compound layer which is formed on a modified portion can suppress moisture absorption, and monatomic

oxygen fill vacancies on the phosphor surface by using introduced gas including fluorine atoms, which makes it possible to suppress time-lapse changes of BAM. Also, fluorine atoms are effective in eliminating impurities included in the process of applying a phosphor on and around the surface and impurities produced in synthesizing.

[0071]

[EFFECTS OF THE INVENTION]

Thus, according to the present invention, it is possible to suppress the time-lapse changes in luminescent characteristics of the phosphor, and to manufacture an illumination device and a plasma display having excellent luminescent characteristics.

[BRIEF DESCRIPTION OF THE DRAWINGS]

FIG.1 is a block diagram of the first embodiment of the present invention.

FIG.2 shows the relationship between heating temperature and chromaticity y of a phosphor.

FIG.3 shows the relationship between heating temperature and luminescence intensity of a phosphor.

FIG.4 is a block diagram of the second embodiment of the present invention.

FIG.5 shows the structure of a conventional plasma display.

[DESCRIPTION OF CHARACTERS]

- 1 reactor vessel
- 2 oxygen gas inlet
- 25 3 phosphor
- 4 processing object on which a phosphor is attached
- 5 sample stage

- 6 UV lamp
- ~~7~~ nitrogen gas inlet
- 8 gas outlet for discharging gas
- 9 ultraviolet light
- 5 10 temperature controller
- 11 UV lamp controller
- 12 fluorinated gas inlet
- 13 front glass substrate
- 14 display electrode
- 10 15 dielectric glass layer
- 16 dielectric protective layer
- 17 rear glass substrate
- 18 address electrode
- 19 barrier ribs
- 15 20 discharge space
- 21 red phosphor layer
- 22 green phosphor layer
- 23 blue phosphor layer

[DOCUMENT] Abstract

20 [ABSTRACT]

[PROBLEM]

The present invention aims to prevent deterioration in a phosphor due to moisture absorption, and to provide a long-life phosphor having a preferable characteristic.

25 [MEANS TO SOLVE THE PROBLEM]

It is possible to fill oxygen vacancies of the phosphor by causing a chemical reaction between the phosphor and ozone and

monatomic oxygen (oxygen radical) by a phosphor treatment method of modifying such that (i) a surface of the phosphor and a vicinity of the surface chemically react with the ozone and the monatomic oxygen with the phosphor exposed to a mixed gas atmosphere including at least ozone, oxygen and monatomic oxygen, and (ii) an oxygen element ratio of the surface of the phosphor and the vicinity of the surface is higher than an oxygen element ratio of the phosphor except for the surface of the phosphor and the vicinity of the surface.

[MEANS TO SOLVE THE PROBLEM]

10 [SELECTED FIGURE] FIG.1

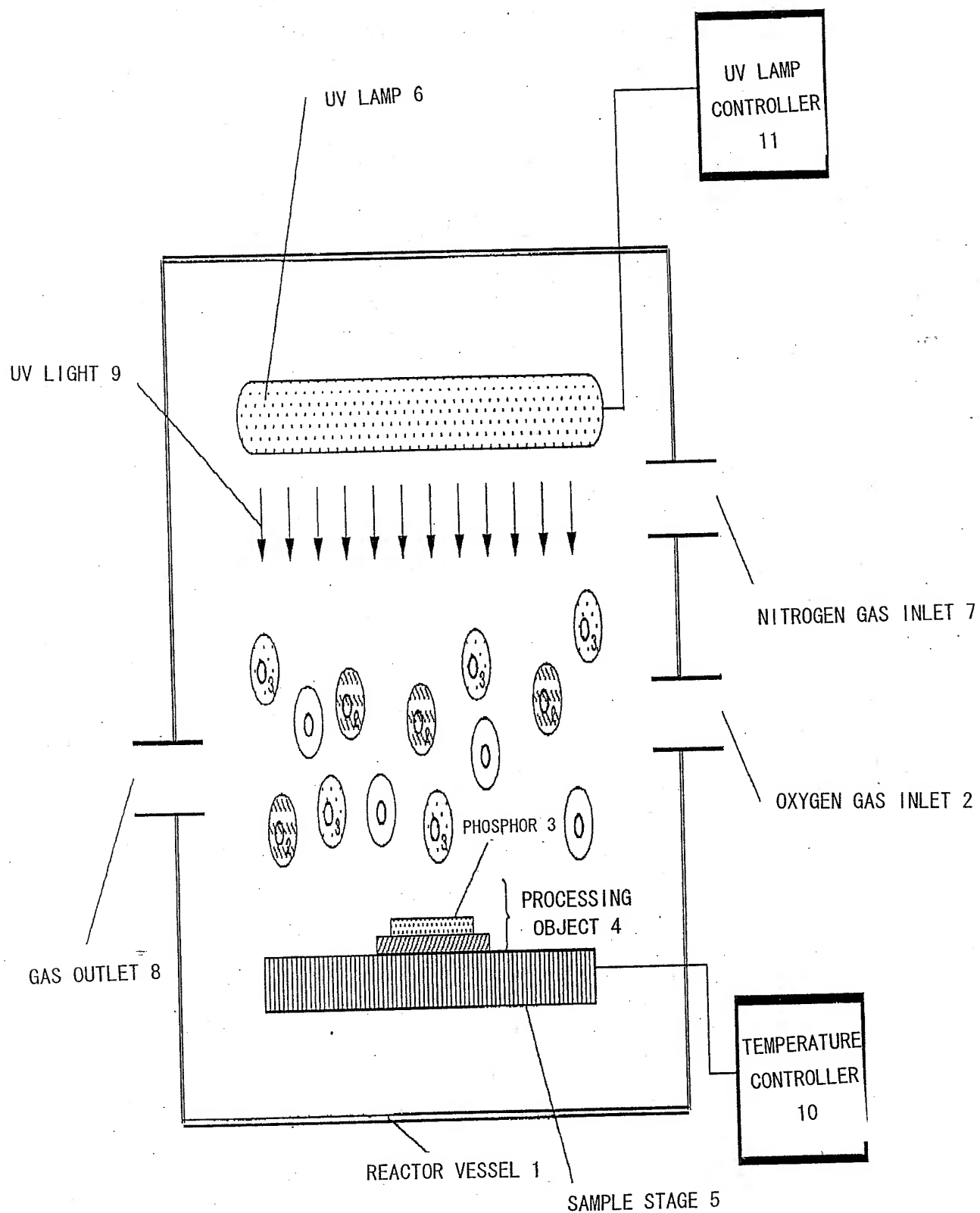


FIG. 2

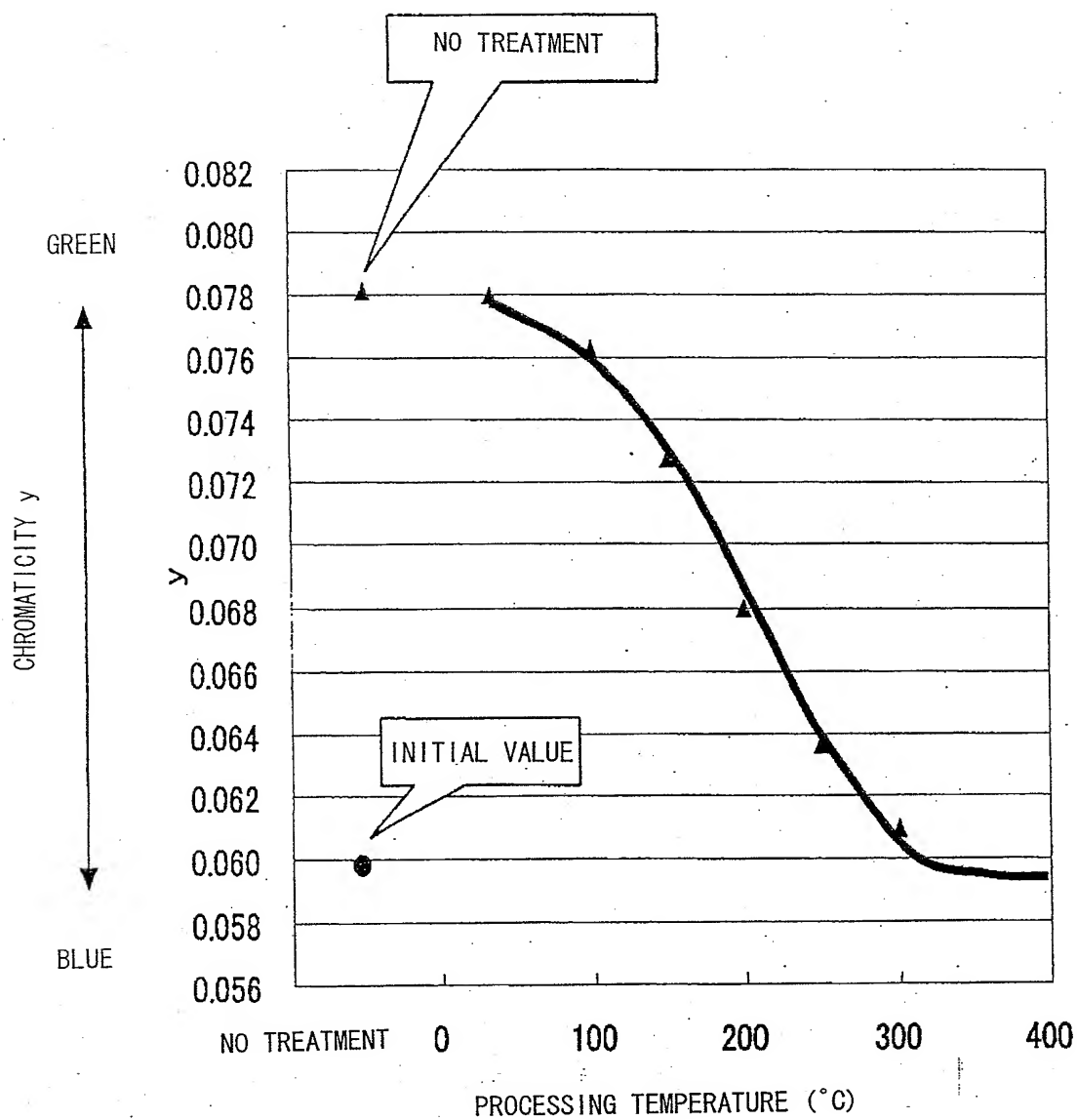


FIG. 3

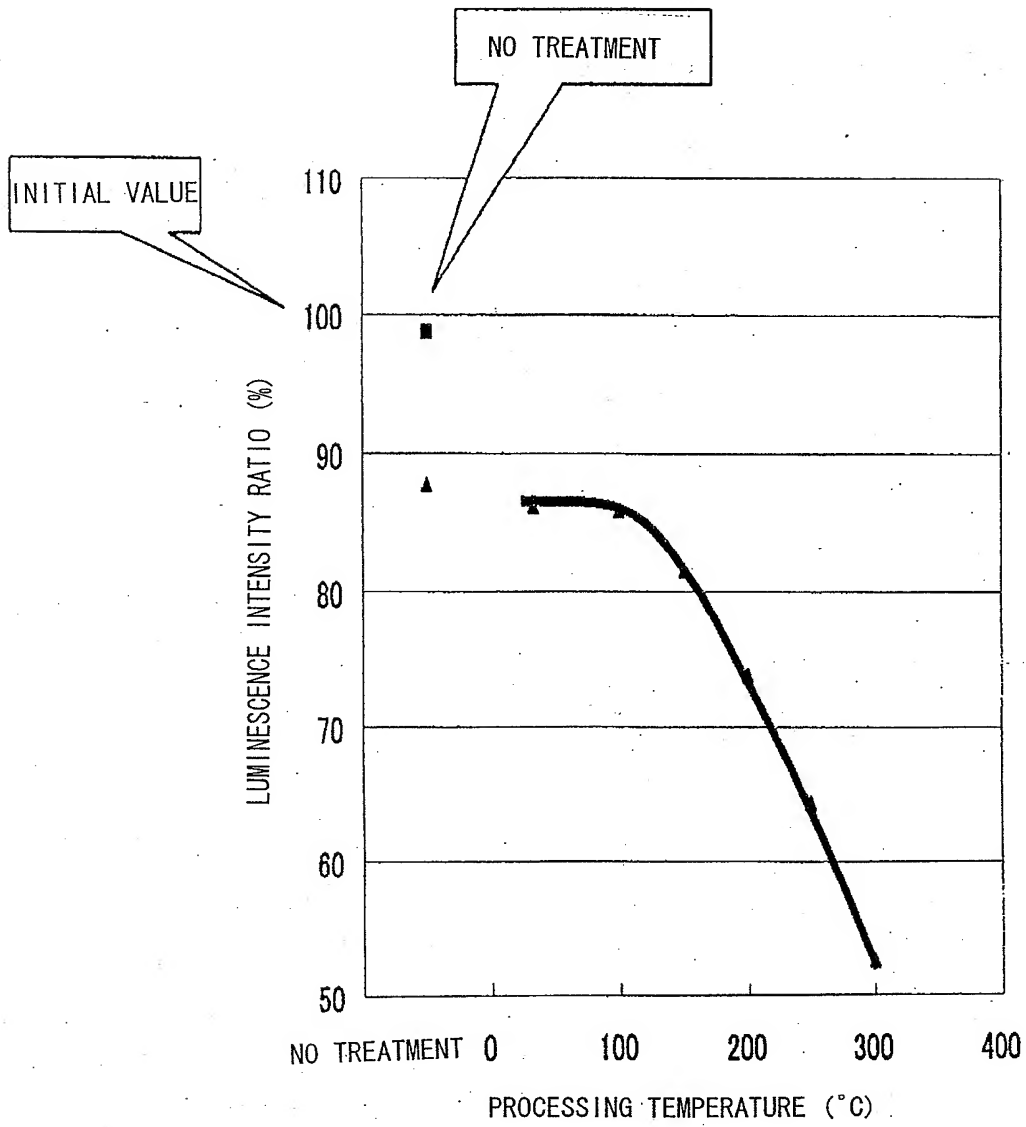


FIG. 4

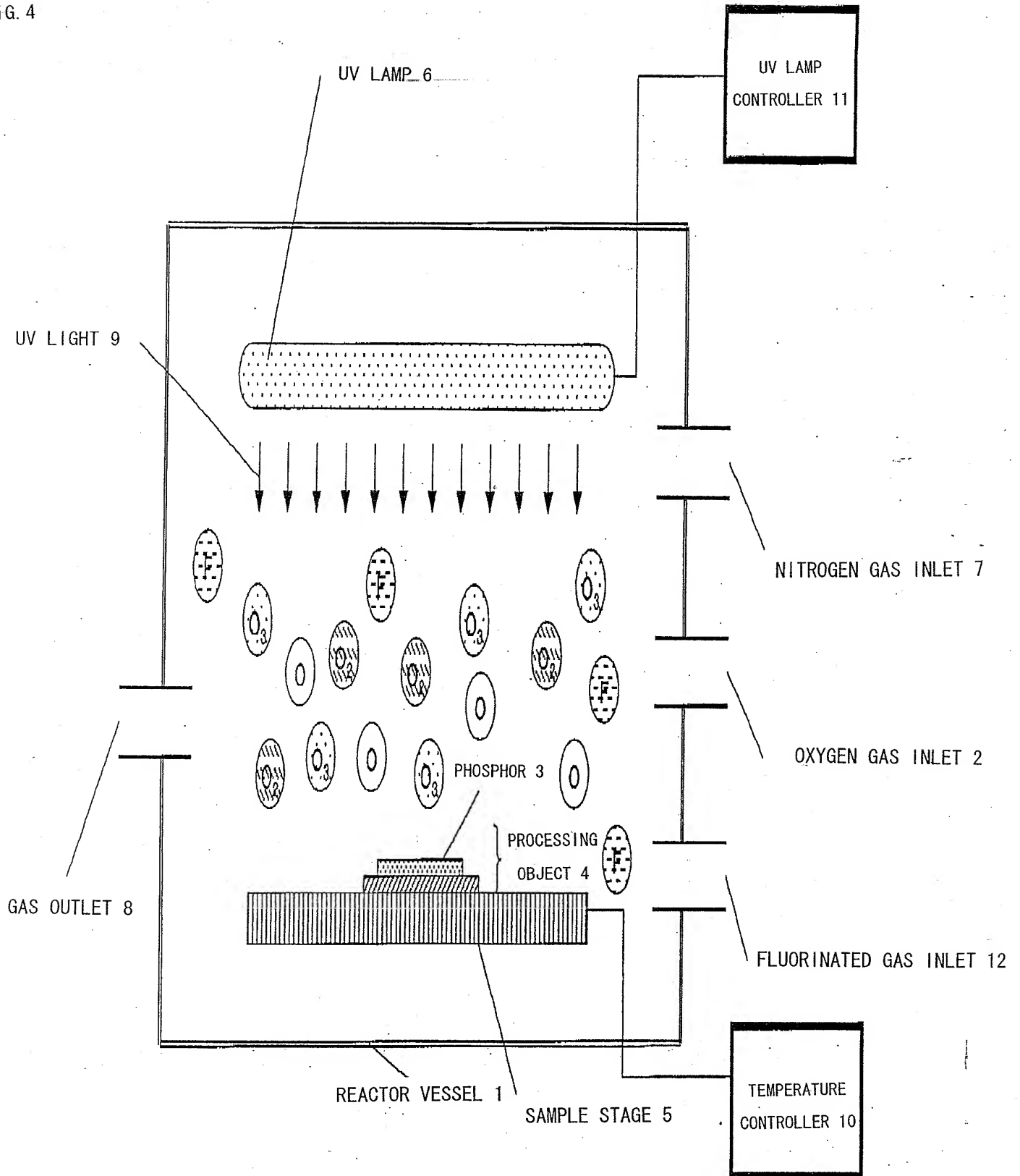


FIG. 5

